Electrocatalytic oxidation of methanol on ordered binary catalyst of manganese and nickel oxide nanoparticles

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C O R R E S P O N D I N G   A U T H O R

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Abstract

The electrooxidation of methanol from alkaline medium at different arrangement of binary catalysts composed of NiO and MnO nanoparticles modified glassy carbon electrode (GC) is studied. Different techniques such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) are used for the characterization of those electrocatalysts. The enhancement of the electrocatalytic oxidation of methanol depends essentially on the arrangement and the loading extent of the NiO nanoparticles. The arrangement in which MnO is deposited first followed by NiO nanoparticles (GC/MnO/NiO) reveals the best performance. The study is performed under different loadings of the NiO catalyst and different concentrations of methanol. Minimum loading of NiO is required to obtain synergism between MnO and NiO. The EIS results confirm the above trends and also help to interpret the above conclusions.

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Introduction

Although numerous studies on direct methanol fuel cell (DMFC) have been published during the last few decades, practical commercialization of DMFCs still faces many challenges such as materials and technical shortcomings. These include high cost of Pt-based electrocatalysts, low electroactivity of methanol oxidation reaction, sluggish kinetics of oxygen reduction reaction and methanol crossover [1,2]. Electrocatalytic oxidation of methanol in alkaline media has attracted more concerns due to its potential application in alkaline anion-exchange membrane fuel cells (AEMFCs) [3–5]. Several benefits have been gained in using AEMFC compared to DMFC with a proton-exchange membrane. These include: more facile methanol oxidation reaction and lower methanol crossover [6,7]. Platinum and Pt-based electrodes are still the most satisfactory electrode materials in DMFCs both for its activity and stability. Thus, Pt anode is an unavoidable candidate for MeOH oxidation.

One of the main problems of Pt electrode is the poisoning resulting from adsorbed intermediate such as COads [8,9]. Poisoning with COads can be alleviated by using a bi-functional mechanism, which provides the electrooxidation of the carbonaceous byproducts via neighboring OHads. Faster removal of the adsorbed carbonaceous species can continuously creates free adsorption sites for methanol molecules, thus resulting in an enhancement of the methanol electrooxidation. Poisoning of Pt catalysts calls for replacement of the Pt with Pt-based alloys such as PtRu and PtNi. Pt-based binary and ternary alloys have shown an enhanced electrocatalytic activity toward MeOH oxidation because of better CO
tolerance of Pt in the alloys [1,10–13]. Many transition metals, such as Sn, Ni and Co [14–16], and metal oxides (MOx), such as CeO2, SnO2, RuO2, WO3, and TiO2, are also used as a promoter or the Pt catalyst support to improve CO tolerance [17–22]. In the present work, we propose the use of both NiOx and MnOx nanoparticles as additives to the Pt electrode in order to obtain better electrocatalytic properties towards MeOH oxidation and high tolerance to CO poisoning. Prior to this step the rule of each catalyst maybe studied here as a separate work.

Nickel oxide (NiOx) has been known of its high tolerance to alcohol oxidation when alloyed with Pt. For instance, an improved activity of methanol oxidation was observed on Pt-rich shell coated Ni particles [23] and a synergistic effect between Ni and Pt was also proposed when used as a catalyst for the MeOH oxidation reaction acidic media [24,25]. The electrocatalytic properties of the metal oxide towards methanol oxidation depend not only on the type of the metal oxide [26] but also on the shape and size of the obtained metal oxide nanoparticles and the substrate which imposes its impacts on the catalytic activity of the oxide [27,28]. NiO is a catalyst for the oxidation of organic compounds but its activity is affected by competing reactions and physical attributes caused by differences in synthesis techniques and the substrate [29–32].

Manganese oxide (MnOx), on the other hand, demonstrates strong synergism with Pt and enhancement of methanol and formic acid oxidation [33,34]. Synergism and bi-functional mechanism are dominant between Pt and the metal oxide. The understanding of the role of such MOx is crucial for better designing of Pt-based binary or ternary catalysts for MeOH oxidation. Since NiOx and MnOx are less expensive and are relatively stable in alkaline media, it is expected to be good additives to Pt. Nevertheless, the role of NiOx and MnOx in promoting methanol oxidation in alkaline media is still not fully discovered and needs to be further studied. It is well documented that metal oxides of Cu, Ni and Mn showed high electrocatalytic performance toward methanol oxidation in alkaline medium due to strong absorbability of methanol molecules on the metal oxide surface. Ni and Ni alloys with other metals such as Cu and Mn have been used for MeOH oxidation [35–37]. The bimetal (Ni and the other metal) was deposited simultaneously on the substrate from a bath containing different ratios of the metal ions. In this context, the use of different orders for deposition of different metal oxides and its impact on MeOH oxidation has not been illustrated yet [38,39].

The purpose of the present work is to fabricate a binary catalyst composed of NiOx and MnOx modified GC with a controlled loading and order of the deposition. Different techniques (CV, EIS and SEM) will be used for the electrochemical and surface characterization. Methanol oxidation will be studied on the different electrodes in alkaline medium. An attempt is introduced to optimize the order of deposition and the loading extent of NiOx.

Fig. 1 – SEM images of (A) GC/NiOx and (B) GC/MnOx/NiOx. EDX chart of GC/MnOx/NiOx is shown in image C.
**Experimental**

**Measurements**

All the reagents used in this work were Merck products of analytical grade and were used without further purifications. Doubly distilled water was used throughout. The working electrode was GC (d = 3.0 mm). It was cleaned by mechanical polishing with aqueous slurries of successively finer alumina powder (down to 0.06 mm) then washed thoroughly with second distilled water. An Hg/Hg2Cl2/KCl (sat) (SCE) and a Pt sheet were used as reference and counter electrodes, respectively. An electrochemical cell with a three-electrode configuration was used in this study. Electrochemical characterizations were performed using system IM6 Zahner elektrik Meßtechnik, Germany. The experimental impedance spectra were fitted with the appropriate equivalent circuits using the “SIM” program included with the IM6 package. The suitability of the elements in the proposed equivalent circuits to fit the experimental data was judged by the error% of the fitting and by comparing the calculated and the experimental impedance plots. The frequency range of 100 kHz to 100 mHz fitting and by comparing the calculated and the experimental suitability of the elements in the proposed equivalent circuits using the “SIM” program included with the IM6 package. The spectra were fitted with the appropriate equivalent circuits.

**Electrode modification**

Modification of GC with NiOx was achieved in two sequential steps. Potentiostatic deposition of metallic nickel on the working electrode (i.e., GC) from an aqueous solution of 0.1 M acetate buffer solution (ABS, pH = 4.0) containing 1 mM Ni(NO3)2·6H2O by applying a constant potential electrolysis of −1 V for different time durations. Then, passivation of the metallic Ni in 0.1 M phosphate buffer solution (PBS, pH = 7) by cycling the potential between −0.5 and 1 V for 10 cycles at a scan rate of 200 mV/s [31,32]. Then modification with MnOx was achieved by cycling the potential from 0 to 0.4 in 0.1 M Na2SO4 containing 0.1 M Mn(CH3COO)2·5H2O for 60 cycles, then activation for 5 cycles in 0.5 M NaOH solution in the potential range −0.2 to 0.6 V. The sequence of the deposition of the two catalysts, i.e., NiOx is deposited first and then MnOx, or vice versa was achieved by keeping the number of MnOx cycles constant at 60 cycles and deposition time of NiOx is changed.

**Results and discussion**

**Surface and electrochemical characterization**

Fig. 1(A and B) shows the SEM images of the modified electrodes. Image A shows typical SEM micrograph of GC/NiOx electrode. It reveals that NiOx is deposited as nanoparticles in a uniform distribution with an average particle size of about 90–100 nm. In image B (GC/MnOx/NiOx sample, MnOx deposited first), NiOx is extensively deposited as compared with image A. It seems also that NiOx partially cover the previously deposited MnOx. Image C (Fig. 1) shows an EDX spectrum of GC/MnOx/

NiOx prepared as mentioned above in the Experimental section. This figure shows the peaks of the manganese and nickel at 5.9 and 7.5 keV in quantities of 5.4 and 0.5 by weight percent, respectively. This sustains that both NiOx and MnOx are exposed in the same sample, and that NiOx does not fully cover the previously deposited MnOx, consistently with the SEM shown as the inset in which the well known porous texture of MnOx is obscured by the subsequent deposition of NiOx.

Fig. 2 shows the CV responses for different electrodes in 0.5 M NaOH. The electrodes are: (a) GC, (b) GC/MnOx, (c) GC/NiOx/MnOx, (d) GC/NiOx, and (e) GC/MnOx/NiOx. The time for loading the NiOx is 10 min and 60 cycles were used for the MnOx deposition. The CV of the GC electrode is featureless and that of the GC/MnOx is a bed-like CV which is known for the low conductivity of MnOx. All the CVs (c–e) reveal the redox peak at ~0.42 V and 0.36 V which correspond to the Ni(II)/Ni(III) redox couples (i.e., Ni(OH)2 + OH− → NiOOH plus; H2O + e−). Note that the above CVs were obtained after subsequent cycles of each electrode in 0.5 M NaOH. The given CV in Fig. 2 is the 20th cycle. The peak potential at the redox couple Ni(II)/Ni(III) is not changed at the different electrodes. The peak current, however, is dramatically affected by the type of the electrode. It was found to be in the order; GC/MnOx/NiOx > GC/NiOx > GC/MnOx/MnOx.

At the GC/NiOx electrode the well-defined redox waves of the surface confined Ni(II)/Ni(III) is observed; the conversion is represented in acid medium by a proton diffusion in which β-NiOOH is likely formed (Eq. (1)), and by solvent mechanism in alkaline medium in which γ-NiOOH is formed through the diffusion of OH− (Eq. (2)).

\[ \text{Ni(OH)}_2 \rightarrow \text{NiOOH} + \text{H}^+ + e^- \]  
\[ \text{Ni(OH)}_2 + \text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} + e^- \]  

It has been reported that β-NiOOH phase enhances the oxidation of organic molecules [40]. The deposition of NiOx on
the GC/MnO$_x$ (i.e., GC/MnO$_x$/NiO$_x$, curve e) is characterized by marked enhancement in the Ni(II)/Ni(III) couple, especially the anodic peak, as compared with the GC/NiO$_x$ electrode (curve c). This may be attributed to the increase of the Ni$^{3+}$ content by doping the NiO$_x$ by MnO$_x$ (Eqs. (3) and (4)), which can convert some of the Ni$^{2+}$ to Ni$^{3+}$ resulting in an increase in the conductivity of the former. This may proceed according to the following reactions; (cf. Methanol electrooxidation section)

$$\text{Mn(IV)} \rightarrow \text{Mn(V)}$$

(3)

$$\text{Mn(V)} + \text{Ni}^{2+} \rightarrow \text{Mn(IV)} + \text{Ni}^{3+}.$$  

(4)

It is noteworthy to mention that the charging current in this case significantly decreases upon the deposition of the NiO$_x$ on the GC/MnO$_x$ electrode. The response obtained at GC/ NiO$_x$ (curve d) in the potential range −0.2 to 0.3 V is almost restored after the deposition of NiO$_x$ onto GC/MnO$_x$. This is certainly due to the deposition of NiO$_x$ onto the previously deposited MnO$_x$. Interestingly the peak current of the Ni(II)/Ni(III) couple significantly decreases when the order of the deposition is reversed, i.e., when MnO$_x$ is deposited onto GC/ NiO$_x$ (GC/NiO$_x$/MnO$_x$, curve c). The last remark points to the partial deposition of MnO$_x$ on the previously deposited NiO$_x$.

**Methanol electrooxidation**

Cyclic voltammograms (CVs) were taken in presence of the MeOH in order to study the impacts of the order of deposition of the oxides, the loading extent of NiO$_x$ and the methanol concentration on the electrocatalytic oxidation of MeOH. Fig. 3 shows CVs for methanol oxidation at (a) GC, (b) GC/MnO$_x$, (c) GC/NiO$_x$/MnO$_x$, (d) GC/NiO$_x$, and (e) GC/MnO$_x$/NiO$_x$ in 0.5 M NaOH containing 0.5 M methanol at a scan rate of 10 mV/s. The figure demonstrates the effect of loading single catalyst of MnO$_x$ or NiO$_x$ and binary catalyst composed of both NiO$_x$ and MnO$_x$ nanoparticles. Methanol oxidation on binary catalyst GC/MnO$_x$/NiO$_x$ reveals the best performance as can be seen from the highest peak current ($I_p$) and the negative shift on the onset potential of the methanol oxidation.

The enhancement of MeOH oxidation on the GC/MnO$_x$/ NiO$_x$ electrode and this increase in $I_p$ can be attributed to different reasons. Of these reasons high adsorbability of MeOH on MnO$_x$, increase of Ni$^{3+}$ and increase of surface concentration for the β-NiOOH form upon deposition of NiO$_x$ on the MnO$_x$ instead of deposition on the GC surface (see discussion on Fig. 2). The increase of anodic current due to methanol oxidation is accompanied by a decrease in the cathodic (backward) current indicating methanol enabled to reduce the entire high valence of nickel species formed in the oxidation cycles.

The figure points to the importance of the order of deposition of NiO$_x$ and MnO$_x$ nanoparticles. For instance, we can see that, when MnO$_x$ deposited first followed by deposition of NiO$_x$, the electrode shows best electrocatalytic enhancement of methanol oxidation. This can be attributed to the higher absorption ability of MnO$_x$ to methanol. The lower currents obtained on GC/NiO$_x$/MnO$_x$ indicate that MnO$_x$ is preferentially deposited on the NiO$_x$ particles. It is noteworthy to mention that the loading extent of NiO$_x$ on both GC and GC/ MnO$_x$ is comparable. It is 0.165 and 0.176 mg cm$^{-2}$ for the GC/ NiO$_x$ and GC/MnO$_x$/NiO$_x$ electrode, respectively (see below). Accordingly, it seems that the enhancement of MeOH oxidation on GC/MnO$_x$/NiO$_x$ compared to GC/NiO$_x$ is not attributed to a possible difference in the loading extent of NiO$_x$ since the difference in activity far overweighs the minor increment of the loading extent on the GC/MnO$_x$/NiO$_x$.

The loading of NiO$_x$ has a significant effect on the activity of GC/NiO$_x$ both in blank and in methanol solution. The loading of NiO$_x$ in mg cm$^{-2}$ for both GC/NiO$_x$ and GC/MnO$_x$/ NiO$_x$ electrodes was estimated from the $I_p$ of the redox evolution (Ni$^{2+}$/free bath) at −1.0 V and $I_p$ of Ni electrodeposition at the same potential from the Ni$^{2+}$/ bath mentioned in the Experimental section. Subtraction of the charge passed for the hydrogen evolution, i.e., Q$_{H_2}$ from the charge passed for the Ni electrodeposition Q$_{Ni}$ was estimated for each time of loading. The loading extent was estimated from Faraday’s law. It was found to be 0.016, 0.040, 0.165, and 0.343 mg cm$^{-2}$ for the GC/NiO$_x$ and 0.022, 0.065, 0.176 and 0.387 mg cm$^{-2}$ for the GC/MnO$_x$/NiO$_x$ electrode. Fig. 4A shows the CV responses for GC/NiO$_x$ electrode in 0.5 M NaOH (blank) at different time of NiO$_x$ loadings; (a) 2, (b) 4, (c) 10 and (d) 20 min. As we can see from the figure, the $I_p$ of the redox Ni(OH)$_2$ ↔ NiOOH, increases and the onset potential shifts to more negative values as the loading extent for Ni deposition increases. This can be considered normal as the Ni$^{3+}$/Ni$^{2+}$ surface concentration increases with the deposited amount of NiO$_x$.

Fig. 4B shows similar CVs as those shown in Fig. 4A but in this case the 0.5 M NaOH contains 0.5 M MeOH at the same electrode (GC/NiO$_x$) with the same loading extents of NiO$_x$ at a scan rate of 20 mV/s. The figure reveals that methanol oxidation is dependent on the loading amount of NiO$_x$ and yet $I_p$ increases with the increase in the loading of NiO$_x$. Also, the
onset potential, $E_{\text{onset}}$ for methanol oxidation shifts to more negative values with the increase in the NiO$_x$ loading. For instance, $E_{\text{onset}}$ is 0.38 and 0.32 V for loading of 2 and 20 min, respectively. We can see that at high loading ($t > 4$ min) the sensitivity to the increase in the $I_p$ for methanol oxidation decreases. For instance $I_p$ increases from $\sim 50$ to $\sim 300$ $\mu$A when the NiO$_x$ loading increases from 2 to 4 min. However, when it increases from 10 to 20 min, $I_p$ increases from $\sim 400$ to $\sim 550$ $\mu$A only. This implies that the surface concentration and not the bulk loading of NiO$_x$ that promotes MeOH oxidation. This is consistent with the previously obtained results on glucose oxidation from alkaline solution using similar catalysts [39].

Fig. 5 shows the CV responses for methanol oxidation on GC/MnO$_x$/NiO$_x$ at different NiO$_x$ loading from 0.5 M NaOH containing 0.5 M MeOH. The general features of Fig. 5 are similar to that in Fig. 4B. As the loading of NiO$_x$ in the GC/MnO$_x$/NiO$_x$ increases, $I_p$ increases. At the GC/NiO$_x$ electrode, the peak current is higher than the corresponding at the GC/MnO$_x$/NiO$_x$ electrode at the same loading of NiO$_x$ when the loading is $< 4$ min. This can be attributed to the fact we need minimum loading of NiO$_x$ in order to make the methanol oxidation efficient. As we discussed above MnO$_x$ does not activate methanol oxidation and yet an optimum amount of NiO$_x$ must be used. Significant amounts of NiO$_x$ are deposited inside MnO$_x$ pores and yet the NiO$_x$ exposure to methanol is weak at loading $< 4$ min. However, at loading $> 4$ min, the peak current of MeOH oxidation at the GC/MnO$_x$/NiO$_x$ is higher than that at GC/NiO$_x$. This implies higher electrocatalytic activity towards MeOH oxidation when the loading of NiO$_x$ exceeding some limit. At this stage of loading a synergism takes place where MnO$_x$ plays an important role by its higher adsorption extent to MeOH and yet a proper loading of NiO$_x$ can support higher rates of MeOH oxidation.

Fig. 6 demonstrates the effect of methanol concentration on the LSV response of GC/MnO$_x$/NiO$_x$ electrode in 0.5 M NaOH at 20 mV/s. The $I_p$ increases with the methanol concentration.
The fact that the rate of MeOH oxidation increases with the [MeOH] indicates that the methanol oxidation at the GC/MnO$_x$/NiO$_x$ is a typical electrocatalytic response. In the inset of Fig. 6, a plot of $I_p$ with [MeOH] is shown. A reasonable straight line is obtained at this concentration range. It can be suggested that the above relation of $I_p$ and [MeOH] is due to a diffusion-controlled process and yet diffusion plays an important role at the present concentration range.

Stability of the above electrocatalysts is an essential issue to be discussed here. Fig. 7 depicts current–time relations for MeOH oxidation from 0.5 M NaOH containing 0.5 M MeOH at a constant potential of 0.53 V. The figure demonstrates that GC/NiO$_x$ electrode reveals higher anodic oxidation currents than the GC/NiO$_x$ electrode at the whole operating time period (~2.5 h). This implies reasonable good mechanical and electrocatalytic stability of the above electrode towards MeOH at the prevailed experimental conditions.

Electrochemical impedance study
The EIS measurements were performed in order to further study the catalytic activity of the studied catalysts towards methanol oxidation. The EIS scans were found to depend on the type of the electrode, methanol concentration and loading extent of nickel oxide. Fig. 8 shows the Nyquist diagram of GC/NiO$_x$ electrode in 0.5 M NaOH containing 0.5 M MeOH at potential of 420 mV at different loadings of NiO$_x$ at the GC/NiO$_x$ electrode. The Nyquist plot shows a semi-circle with a diameter depends on the loading extent of the NiO$_x$. The diameter decreases with the increase in the NiO$_x$ loading. Analysis of the experimental spectra was made by best fitting to a corresponding equivalent circuit that is corresponding to the EIS results as shown in the inset of Fig. 8. The equivalent circuits shows; $R_a$, CPE and $R_{ct}$ which represent the solution resistance, a constant phase element corresponding to the double layer capacitance and the charge-transfer resistance associated with the oxidation of methanol, respectively. Thales software provided with the workstation where the dispersion formula suitable to each model was used [41].

To present a satisfactory impedance simulation of the data in Fig. 8, it is important to replace the capacitor, C with a constant phase element (CPE) in the equivalent circuit. This CPE is denoted as $Q_{dl}$ in Tables 1 and 2. This approach is accepted in literature and was attributed to microscopic roughness which causes an inhomogeneous distribution in solution resistance and in the capacitance of the double layer [42]. The impedance ($Z_{CPE}$) of a constant phase element is defined as $Z_{CPE} = [C(j\omega)^a]^{-1}$, where $-1 \leq \alpha \leq 1$, $j = (-1)^{1/2}$, $\omega = 2\pi f$ is the angular frequency in rad/s, $f$ is the frequency in Hz = s$^{-1}$, $\alpha$ is a fitting parameter which is an empirical exponent varies between 1 for a perfect capacitor and 0 for a perfect resistor. In this complex formula an empirical exponent ($\alpha$) varying between 0 and 1, is introduced to account for the deviation from the ideal capacitive behavior due to surface heterogeneity, roughness factor and adsorption effects [41–43]. In all cases, good agreement between theoretical and experimental data was obtained for the whole frequency range with an average error of 3%. The estimated parameters are given in Tables 1 and 2. The $\alpha$ values obtained from the fitting procedures for GC/NiO$_x$ and GC/MnO$_x$/NiO$_x$ are ranged between 0.75 and 0.85. This means that both oxide electrodes do not behave as
perfect capacitor. Meanwhile, the results show that the phase angle has values less than 90° (θ = 55°–70°) which gives more confirmation for the non-ideality of the capacitive behavior of the oxides. At this potential (E = 420 mV), the methanol oxidation is kinetically (charge-transfer) controlled and hence Rct can be obtained from the EIS data. This means that as loading time increases, the impedance decreases and conductivity increases. This confirms well the increase in the peak current obtained from CV responses shown in Fig. 4b.

Fig. 9 shows the Nyquist diagram of GC/MnOx/NiOx electrode in 0.5 M NaOH containing 0.5 M MeOH at potential of 420 mV at different loadings of the NiOx. The features of this Nyquist plot are similar to those of the GC/NiOx electrode shown in Fig. 8. The data shown in Table 1 demonstrates that Rct decreases as the loading of NiOx increases. At loading <4 min, the values of Rct at the GC/NiOx are lower than that at the GC/MnOx/NiOx. At loading >4 min, the Rct values are comparable at both electrodes. These results are comparable with the results obtained from the CVs of both electrodes for MeOH oxidation at different NiOx loadings (Figs. 4b and 5). A minimum loading of NiOx is required to obtain such enhancement of the catalytic oxidation of methanol on GC/MnOx/NiOx.

Fig. 10A presents the Nyquist diagrams of GC/MnOx/NiOx (10 min) electrode at 420 mV both in absence and presence of methanol in 0.5 M NaOH. In the absence of methanol, a semi-circle was obtained. Upon using methanol concentrations ranging from 0.2 to 0.7 M, a steady decrease in the diameter of the semi-circle was observed. An equivalent circuit compatible with the results is shown in the inset of Fig. 10A. Table 2 shows the EIS data obtained upon fitting the EIS experiential data with the equivalent circuit. The results in Fig. 10A and the data in Table 2 demonstrate that as the methanol concentration increases, the Rct decreases. This is in accordance with the CV results discussed in Fig. 6. Fig. 10B shows a Bode diagram corresponding to the Nyquist diagram shown in Fig. 10A above. The results of Bode support the above conclusions especially the fact that the Nyquist plot consists of a semi-circle with a charge-transfer controlled process. The EIS results enabled us to confirm and interpret the CV results obtained above in the previous section.

According to the high current response towards methanol oxidation and also the fact that the oxidation peak for methanol oxidation obtained at a potential much more positive than that of the oxidation of Ni(OH)2, we assume that part of the anodic current is due to methanol oxidation by NiOOH due to the disappearance of the NiOOH reduction peak in the negative sweep and part of the current is due to methanol oxidation on

<table>
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Fig. 9 — Nyquist plot of GC/MnOx/NiOx electrode at different loadings of NiOx in 0.5 M NaOH containing 0.5 M MeOH at 420 mV. The inset shows the equivalent circuit used for fitting of EIS data.

Fig. 10 — (A) Nyquist plot of GC/MnOx/NiOx electrode at different MeOH concentrations in 0.5 M NaOH at 420 mV. The inset shows the equivalent circuit used for fitting of EIS data. The corresponding Bode diagram is shown in (B).
the surface of oxide layer by direct electrooxidation. The redox transition of Ni$^2+/Ni^{3+}$ couple is [44];

$$\text{Ni}^{2+} \rightarrow \text{Ni}^{3+} + e^- \quad (5)$$

and methanol is oxidized on the modified surface via the following reaction

$$\text{Ni}^{3+} + \text{methanol} \rightarrow \text{Ni}^{2+} + \text{intermediate} \quad (6)$$

Eqs. (6) and (7) are according to Fleischmann mechanism [45] and in Eqs. (8) and (9), Ni$^{3+}$ used as active surface for methanol oxidation. Observation of a new oxidation peak for methanol oxidation at a potential much more positive than that of the oxidation of Ni(OH)$_2$ potential is according to Eqs. (8) and (9).

$$\text{Ni}^{3+} + \text{methanol} \rightarrow \text{Ni}^{3+} - \text{intermediate} + e^- \quad (8)$$

$$\text{Ni}^{3+} - \text{intermediate} \rightarrow \text{Ni}^{3+} - \text{products} + e^- \quad (9)$$

Conclusions

The effect of the order for deposition of NiO$_x$ and MnO$_x$ nanoparticles on the electrocatalytic activity towards methanol oxidation was studied using different techniques. The order of loading and loading extent of NiO$_x$ was found to have a dramatic effect. The best catalytic activity was of GC/MnO$_x$ (i.e., MnO$_x$ is deposited first). A synergism was suggested between NiO$_x$ and MnO$_x$ and this synergism was attributed mainly to the higher adsorbability of MeOH on MnO$_x$. It was found that there is an optimum minimum loading of NiO$_x$ on GC/MnO$_x$/NiO$_x$ in order to obtain higher rates of MeOH oxidation. The EIS measurements supported the CV responses and the extracted parameters helped to discuss the catalytic activity of GC/MnO$_x$/NiO$_x$.

References


